

^{13}C NMR Study on Zero-Gap State in the Organic Conductor $\theta\text{-(BEDT-TTF)}_2\text{I}_3$ under Pressure

KAZUYA MIYAGAWA, MOTOAKI HIRAYAMA, MASAFUMI TAMURA¹, AND KAZUSHI KANODA

Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

¹ *Department of Physics, Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan*

We present the results of our ^{13}C NMR study of the quasi-two-dimensional organic conductor $\theta\text{-(BEDT-TTF)}_2\text{I}_3$ under pressure, which is suggested to be a zero-gap conductor by transport measurements. We found that NMR spin shift is proportional to T and that spin-lattice relaxation rate follows the power law T^α ($\alpha = 3 \sim 4$), where T is the temperature. This behavior is consistent with the cone-like band dispersion and provides microscopic evidence for the realization of the zero-gap state in the present material under pressure.

KEYWORDS: zero-gap conductor, NMR, $\theta\text{-(BEDT-TTF)}_2\text{I}_3$, pressure

Graphene provides a unique two-dimensional electron system with a cone-shaped dispersion relation, where quasi-particles are massless Dirac fermions and show an anomalous quantum magneto-transport such as an unconventional quantum Hall effect.¹ The quasi-two-dimensional organic conductor $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$ ($\alpha\text{-I}_3$) under pressure is a candidate bulk version of purely two-dimensional graphene. This material is a charge-ordered insulator below 135 K at ambient pressure.² However, Tajima *et al.* found that the system shows temperature-insensitive resistivity at high pressures above 15 kbar.³ Their subsequent measurements of Hall coefficient indicates its strong temperature dependence over several decades from room temperature down to 1 K.³ Based on these two transport characteristics, they argued that carrier density decreases to a vanishingly small value and that mobility conversely increases to a high value on order of $10^5 \text{ cm}^2/\text{Vs}$ with power-law temperature dependences.³ The band structure of $\alpha\text{-I}_3$ was first calculated by the tight-binding method for the extended Hückel orbital by Kobayashi *et al.* and shown to be semi-metallic with hole and electron pockets at ambient pressure.⁴ Recent calculations by Ishibashi *et al.*,⁵ Kino and Miyazaki,⁶ and Katayama *et al.*⁷ have shown that the variation of transfer integrals and/or inter-site Coulomb interaction with pressure gives a cone-like band-structure and explains the above-mentioned properties of $\alpha\text{-I}_3$ at high pressures.

The same transport characteristics as those of $\alpha\text{-I}_3$ were found in the analogous compound $\theta\text{-(BEDT-TTF)}_2\text{I}_3$ ($\theta\text{-I}_3$) with a similar structure to $\alpha\text{-I}_3$ (Figs. 1(b) and 1(c)).^{8,9} At ambient pressure, $\theta\text{-I}_3$ is a metal¹⁰ in contrast to $\alpha\text{-I}_3$, which is a charge-ordered insulator.² At pressures above 5 kbar, however, $\theta\text{-I}_3$ shows temperature-insensitive resistivity^{8,9} and temperature-sensitive Hall coefficient.⁹ Thus, there have been reports on an increasing number of experiments and theoretical works that support the notion that the organic compound is a bulky material with massless Dirac fermions. However, experimental studies have been restricted to transport measurements to date.

In the present work, we aim at clarifying a possible

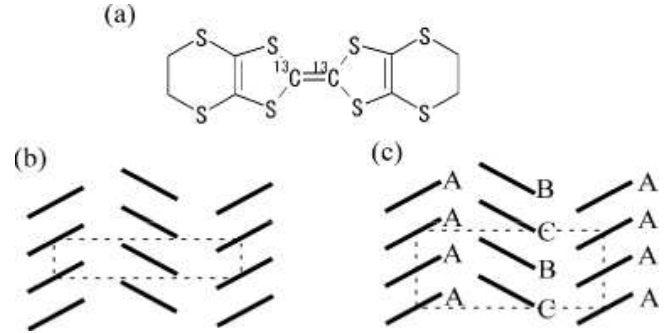


Fig. 1. (a) ^{13}C enriched BEDT-TTF molecule. In-plane BEDT-TTF molecular arrangements in (b) $\theta\text{-I}_3$ (the so-called average structure, where all molecules are equivalent) and (c) the $\alpha\text{-I}_3$ (three BEDT-TTF sites labeled A, B, and C in the unit cell are inequivalent).

graphene-like state in a bulky organic material by the method of nuclear magnetic resonance (NMR). As a sample, $\theta\text{-I}_3$ is adopted because it has the advantage over $\alpha\text{-I}_3$ that experiments can be carried out at much lower pressures.

Here, we perform a ^{13}C NMR experiment on $\theta\text{-I}_3$ under pressure to examine the possible bulky zero-gap state from the magnetic point of view for the first time.

In the present NMR study, we used a $\theta\text{-I}_3$ single crystal where the two central carbon sites connected with a double bond in the BEDT-TTF molecule are substituted with a ^{13}C isotope (Fig. 1(a)). The central carbon sites are located in the region of high density of the highest occupied molecular orbital (HOMO). In accordance with the transport results suggesting that the zero gap state is realized above 5 kbar,^{8,9} we applied a hydrostatic pressure of 8 kbar to the sample using a NiCrAl-BeCu hybrid piston cylinder cell with a pressure-transmitting medium oil, Daphne 7373. We mounted the sample in a NMR coil and applied a magnetic field of 8 Tesla parallel to the conducting plane to eliminate the magneto-orbital effect,¹¹ which is interesting but is out of the scope of the present study. It is noted that the alignment is not perfect; therefore, the sample may be slightly deviated

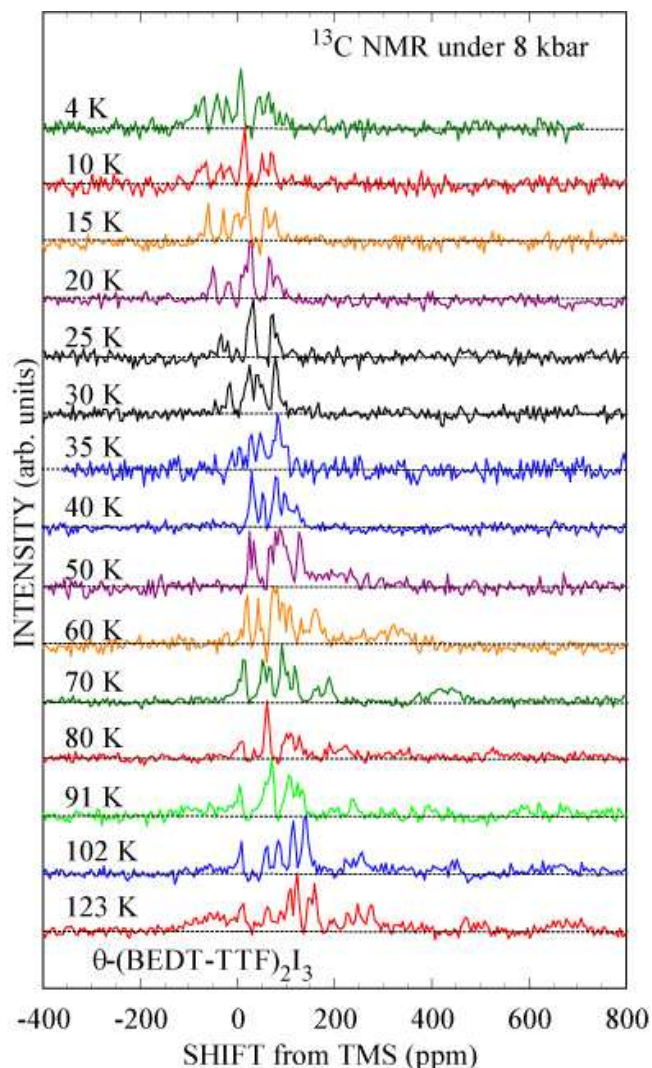


Fig. 2. (Color online) Temperature dependence of ^{13}C NMR spectra.

from the parallel condition. ^{13}C NMR measurement was carried out by the spin-echo method, where the typical width of the $\pi/2$ pulse was $2\ \mu\text{s}$. The NMR spectra were obtained by the first Fourier transformation (FFT) of spin echoes. The ^{13}C NMR frequency of tetramethylsilane (TMS) was used as the origin of the NMR shift. The nuclear spin-lattice relaxation rate $1/T_1$ was obtained by the standard saturation recovery method.

Relaxation curves of ^{13}C nuclear magnetization were fitted to single exponentials for all the temperatures measured.

The temperature dependence of ^{13}C NMR spectra is shown in Fig. 2. The line at approximately -60 ppm at 123 K comes from the pressure medium oil. This line broadens at low temperatures owing to the solidification of oil and becomes unobservable below 100 K because the relaxation time T_1 is much longer than that of the sample. The NMR spectrum of the sample has a rather complicated shape, which consists of many peaks. This spectral feature is different from the simple four-line structure observed at ambient pressure,¹² where the system is an ordinary metal with cylindrical Fermi surfaces,

as evidenced by *de Haas-van Alphen* oscillations.¹³ The four lines are what is expected in the so-called average structure of $\theta\text{-I}_3$ (Fig. 1(b)) determined by XRD analysis¹⁴ at ambient pressure; the two (crystallographically equivalent) BEDT-TTF molecules in the in-plane unit cell are inequivalent with respect to the magnetic field parallel to the conducting layer. Within the molecule, two neighboring ^{13}C atoms, which are equivalent in $\theta\text{-I}_3$, give the so-called Pake doublet due to the nuclear dipolar splitting in the BEDT-TTF molecule. Thus, a total of four lines are expected. The complicated lines show that the structure at 8 kbar is changed from that at ambient pressure. Although the crystal structure under pressure is not known, the pressure dependence of resistivity at room temperature shows a discontinuous jump at approximately 5 kbar^{8,9} above which the transport behavior of the zero-gap conductor, as observed in $\alpha\text{-I}_3$, appears instead of the metallic behavior at ambient pressure. Therefore, we speculate that $\theta\text{-I}_3$ undergoes structural transformation to a phase similar to $\alpha\text{-I}_3$, which has a similar fish bone like molecular arrangement. If the α -type arrangement appears above 5 kbar, the unit cell should contain three kinds of non-equivalent BEDT-TTF molecules (Fig. 1(c)). They are specified by two *A* molecules, and one each of the *B* and *C* molecules, which form two types of columns. It is well known that the nuclear dipole-dipole interaction ($^{13}\text{C}=^{13}\text{C}$) brings a maximum of 4 lines in the case that the neighboring ^{13}C atoms are inequivalent as in the *A* molecule of $\alpha\text{-I}_3$. Thus, the complicated NMR line shape can be explained by the non-equivalent circumstances of BEDT-TTF molecules like the α -type arrangement and dipole-dipole interactions between ^{13}C nuclei in BEDT-TTF.

With decreasing temperature, the NMR spectra shift to a lower frequency and the distribution of resonance frequency becomes smaller, which indicates a decrease in spin susceptibility. Figure 3 shows the temperature dependence of the gravity of NMR spectra, that is, an average shift. It monotonically decreases below 60 K and is proportional to temperature below 40 K. The linear extrapolation of the observed shift to 0 K yields -13 ppm. It is interesting that the linearity holds down to the lowest temperature measured of 4 K. In the BEDT-TTF molecule, the orbital angular momentum is quenched because of its low structural symmetry; so the orbital component of the shift is negligible. In addition, although a possible large diamagnetism expected from the interband effect in the zero-gap state has been theoretically pointed out,¹¹ its contribution to the line shift should be very small in the parallel-field configuration. Thus, the observed line shift is considered to be the sum of a temperature-independent chemical shift and a linearly temperature-dependent spin shift.

The temperature dependence of $1/T_1$ is shown in Fig. 4. T_1 was determined from the recovery curve of the entire spectra, which was well approximated to a single exponential function up to 90% recovery. Because the multiple-peak structure in the spectra indicates the presence of different hyperfine tensors, one expects a non-single exponential recovery curve. A possible explanation for the observed single-exponential nature is in terms of

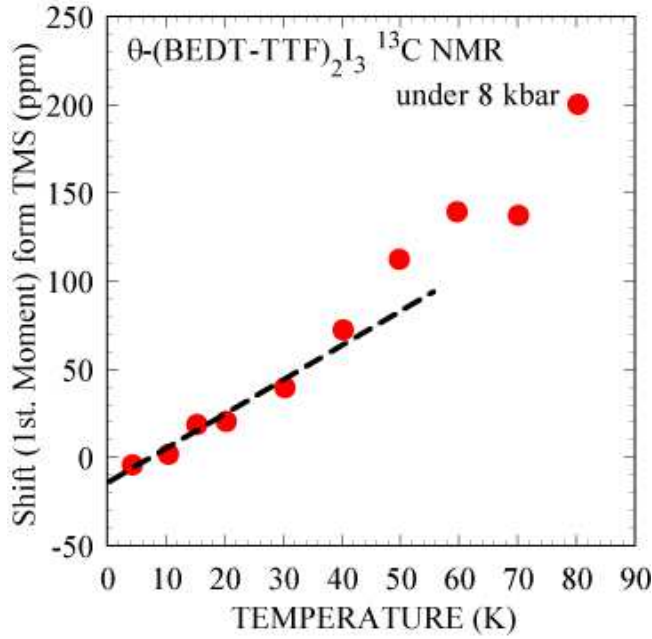


Fig. 3. (Color online) Temperature dependence of ^{13}C NMR shift. The scale of the shift is relative to the line position of TMS.

the T_2 process; when T_1 is much longer than T_2 , the nuclear spin temperatures at different ^{13}C sites reach equilibrium much faster than the nuclear spin-lattice relaxation time. As seen in the figure, $1/T_1$ shows a steep decrease down to 10 K. The temperature dependence seems to be characterized by a power law of T^3 below 30 K with an upward deviation at higher temperatures. An exponential function fails to fit to the data.

It is evident that these behaviors of the line shift and $1/T_1$ are not expected in conventional metals.

It is well known that in a simple metallic case, the spin shift and $1/(T_1T)$ are proportional to the density of states averaged by temperature, $\langle D(\epsilon) \rangle_{kT}$ and $\langle D(\epsilon) \rangle_{kT}^2$, respectively, where ϵ is the energy measured from the Fermi energy, ϵ_F . Because $\langle D(\epsilon) \rangle_{kT}$ is essentially temperature independent in a simple metal, the spin shift and $1/(T_1T)$ would be temperature-independent. The qualitatively different behaviors observed here are explained in terms of the cone-shaped band dispersion (Dirac cone) with a Fermi level at the apex. The low-energy quasi-particle excitations around the apex of the Dirac cone, which governs the magnetic properties, have $D(\epsilon)$ with a linear ϵ dependence. In this case, the thermal average of the density of states, $\langle D(\epsilon) \rangle_{kT}$, is proportional to temperature. This leads to the following relations: spin shift $\propto \langle D(\epsilon) \rangle_{kT} \propto T$ and $1/(T_1T) \propto \langle D(\epsilon) \rangle_{kT}^2 \propto T^2$, as in the case of quasi-particle excitations in d -wave superconductivity. The observed power law behaviors in shift and $1/T_1$ are consistent with this zero-gap nature. The upward deviation of $1/(T_1T)$ from the T^2 dependence above 30 K may be related to the electron correlation effect or van-Hove singularity predicted to be located at a higher energy but remains to be seen.⁶

As encountered in graphene with a similar band dispersion, impurity works as a dopant and easily shifts

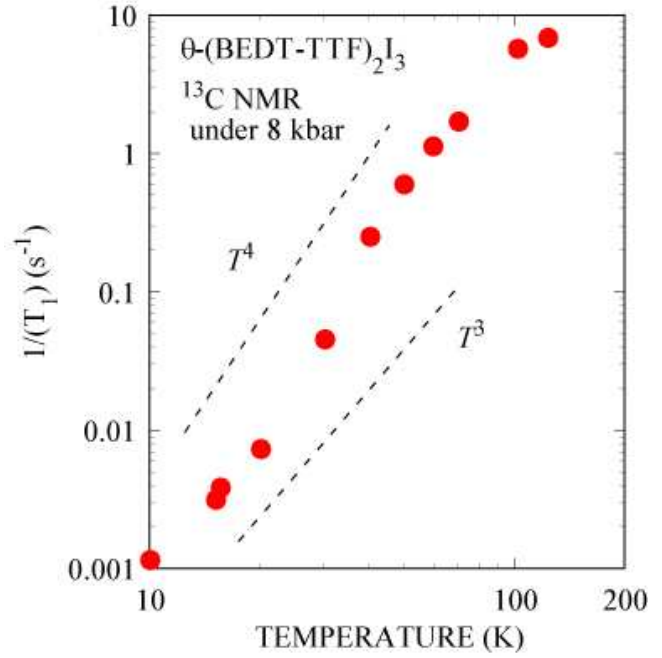


Fig. 4. (Color online) ^{13}C nuclear spin-lattice relaxation rate.

the Fermi level on the order of 10 meV¹⁵ because of the vanishingly small density of states near the Dirac apex. For $\alpha\text{-I}_3$, the sign reversal of Hall coefficient is often observed at approximately 2 ~ 7 K¹⁶ and is interpreted in terms of the passage of chemical potential across the Dirac apex¹¹ as a manifestation of doping due to possible defects in the I_3^- lattice. If the Fermi level is shifted from the cone apex, $\langle D(\epsilon_F) \rangle_{kT}$ should yield a finite value, giving $1/(T_1T) = \text{constant}$ in the low-temperature limit. The persistence of $1/(T_1T) \propto T^2$ down to 10 K, at least in the present observation, means that the Fermi level shift is smaller than 1 meV.

In conclusion, the magnetism of $\theta\text{-(BEDT-TTF)}_2\text{I}_3$, under pressure has been investigated by ^{13}C NMR study. The linear temperature dependence of spin shift and the squared temperature dependence of $1/(T_1T)$ are both consistent with the picture that this material is a bulk zero-gap conductor.

The authors thank N. Tajima, A. Kobayashi, S. Katayama, Y. Suzumura, A. Kobayashi, H. Kobayashi, and H. Fukuyama for helpful discussion. This work is partially supported by Grant-in-Aids for Scientific Research on Priority Area (No. 17071003) and on Innovative Area (No. 20110002) from MEXT, by Grant-in-Aids for Scientific Research (A) (No. 20244055) and (C) (No. 20540346) from the JSPS, and by the Global COE Program: Global Center of Excellence for the Physical Sciences Frontier (No. G04).

- 1) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonosand, and A. A. Firsov: *Nature* **438** (2005) 197; Y. Zhang, Y. W. Tan, H. L. Stormerand, and P. Kim: *Nature* **438** (2005) 201.
- 2) H. Kino and H. Fukuyama: *J. Phys. Soc. Jpn.* **64** (1995) 1877; H. Seo: *J. Phys. Soc. Jpn.* **69** (2000) 805; Y. Takano, K. Hiraki, H. M. Yamamoto, T. Nakamura, and T. Takahashi: *J.*

- Phys. Chem. Solids **62** (2001) 393; R. Wojciechowski, K. Yamamoto, K. Yakushi, M. Inokuchi, and A. Kawamoto: Phys. Rev. B **67** (2003) 224105.
- 3) N. Tajima, M. Tamura, Y. Nishio, K. Kajita, and Y. Iye: J. Phys. Soc. Jpn. **69** (2000) 543; N. Tajima, S. Sugawara, M. Tamura, Y. Nishio, and K. Kajita: J. Phys. Soc. Jpn. **75** (2006) 051010; N. Tajima, S. Sugawara, M. Tamura, R. Kato, Y. Nishio, and K. Kajita: Eur. Phys. Lett. **80** (2007) 47002.
- 4) A. Kobayashi and H. Kobayashi: private communication.
- 5) S. Ishibashi, T. Tamura, M. Kohyama, and K. Terakura: J. Phys. Soc. Jpn. **75** (2006) 015005.
- 6) H. Kino and T. Miyazaki: J. Phys. Soc. Jpn. **75** (2006) 034704.
- 7) S. Katayama, A. Kobayashi, and Y. Suzumura: J. Phys. Soc. Jpn. **75** (2006) 054705.
- 8) M. Tamura, F. Matsuzaki, N. Tajima, Y. Nishio and K. Kajita: Synth. Met. **86** (1997) 2007.
- 9) N. Tajima, A. Tajima, M. Tamura, R. Kato, Y. Nishino, and K. Kajita: J. Phys. IV France **114** (2004) 263.
- 10) H. Kobayashi, R. Kato, A. Kobayashi, Y. Nishio, K. Kajita, and W. Sasaki: Chem. Lett. **1986** (1986) 789; R. Kato, H. Kobayashi, A. Kobayashi, Y. Nishio, K. Kajita, and W. Sasaki: Chem. Lett. **1986** (1986) 957.
- 11) A. Kobayashi, Y. Suzumura, and H. Fukuyama: J. Phys. Soc. Jpn. **77** (2008) 064718.
- 12) M. Hirata: private communication.
- 13) M. Tokumoto, A. G. Swanson, J. S. Brooks, M. Tamura, H. Tajima, and H. Kuroda: Solid State Commun. **75** (1990) 439.
- 14) A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki: Chem. Lett. **1986** (1986) 2017.
- 15) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov: Science **306** (2004) 666.
- 16) N. Tajima: private communication.